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The Determination of Antimony, Arsenic, Beryllium, Cadmium, Lead, Selenium, Silver and Tellurium in Environmental Water Samples by Flameless Atomic Absorption

Environmental Protection Agency, Chicago, Ill.

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ANALYTICAL METHOD, PROCEDURE AND EVALUATION RELATIVE TO THE REFEREE METHOD SUBMITTED FOR APPROVED USE IN THE NATIONAL POLLUTION DISCHARGE ELIMINATION SYSTEM (NPDES) AS SPECIFIED BY THE OCTOBER 16, 1973 FEDERAL REGISTER

THE DETERMINATION OF ANTIMONY, ARSENIC, BERYLLIUM, CADMIUM, LEAD, SELENIUM, SILVER AND TELLURIUM IN ENVIRONMENTAL WATER SAMPLES BY FLAMELESS ATOMIC ABSORPTION

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16. ABSTRACT

Analytical procedures for measuring concentrations of the title metals in environmental samples are described. Results obtained using the flameless atomic absorption procedures are compared to data obtained using the referee method as defined in the October 16, 1973, Federal Register. It is concluded that the flameless atomic absorption methods are equivalent or superior to the referee procedure for these metals.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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1. SCOPE AND APPLICATION

This method is applicable to all surface and drinking waters, domestic and industrial wastes at all concentration levels normally found, with appropriate dilutions, for the elements listed in Table I. Appropriate linear ranges based on a 50 ul sample volume are also presented in Table I.

2. SUMMARY OF METHOD

Sample aliquots are introduced into a graphite furnace of the mini-Massman design. Separate drying, charring and atomizing program steps are incorporated in a controller that establishes appropriate resistence heating of the graphite tube. This unit is used with a double beam Perkin-Elmer* atomic absorption spectrophotometer equipped with a deuterium background corrector. The decrease in energy of the hollow cathode or electrodeless discharge lamp (EDL) is detected on a strip chart recorder as a transient peak and this peak height is proportional to concentration within the ranges given in Table I.

3. SAMPLE HANDLING AND PRESERVATION

Samples are collected in high density polyethylene containers and are preserved with concentrated nitric acid at a concentration of 0.5%. Reagent blanks are provided with each set of samples so that net metal concentrations can be reported.

4. INTERFERENCES

4.1 Broad Band Absorption - This interference occurs when another component of a sample matrix is volatilized simultaneously with the element of interest and results in an output that masks, or that may be mistaken for, the signal from that element. This false response may be caused by molecular absorption and/or light scatter by interfering constituents. High boiling mineral

acids, i.e. sulfuric, phosphoric, cannot be used with the HGA-2000 Perkin-Elmer furnace, since these acids have a tendency to recondense in the cooler regions of the graphite tube during the charring cycle and are revolitilized into the light beam during the atomization step producing an interfering signal. In order to eliminate or minimize the non-specific absorption the need for simultaneous background correction as a function of sample matrix must be carefully evaluated by visual monitoring of the signal on the energy meter. In this application, simultaneous background correction is used for the determination of antimony, arsenic, cadmium, lead, selenium, and tellurium, and is not required for beryllium and silver.

4.2 Chemical - This interference originates from compound formation by matrix components with elements of interest at the atomization temperature, thus reducing the free atom population of the element determined. As a consequence, sensitivities are generally not invariant as is apparent from representative standard addition curves in Figures 1 through 6. Therefore, the following measures are taken in order to reduce this potential interference.

4.2.1 Acidities in samples and standards must be controlled as to acid type and concentration.

4.2.2 Sample volumes analyzed must be identical.

4.2.3 The standard additions approach must be used for the determination of element concentrations.

4.3 Contamination - The inherent absolute sensitivity of the furnace technique imposes severe restrictions on the cleanliness of laboratory-ware and the purity of reagents. Great care must be exercised in these areas to insure valid analytical results.

5. APPARATUS

5.1 Atomic Absorption Spectrophotometer - Any double beam Perkin-Elmer instrument, modified with the appropriate optical beam retrofit kit, and equipped for simultaneous deuterium arc background correction, is satisfactory. The Perkin-Elmer HGA-2000 or HGA-2100 graphite furnaces are acceptable. Perkin-Elmer hollow cathodes or EDLs are used as the emission line source.

5.2 Recorder - Any commercial strip chart recorder having a full-scale response of 0.5 sec. is satisfactory.

5.3 Pipets - Eppendorf type pipets with polypropylene tips are suitable for sample injection. The absence of metal contaminants in the tips should be verified experimentally prior to use.

5.4 Glassware - All glassware in this procedure must be cleaned with 8N nitric acid and rinsed with distilled, deionized water.

5.5 Gases - Prepurified grade nitrogen or argon are satisfactory carrier gases.

6. REAGENTS

6.1 Water - Distilled, deionized water was found to be acceptable. The supply should, however, be analyzed for metals of interest prior to use.

6.2 Acid - Ultrex grade (Baker Chem. Co.) or distilled nitric acid have been found to be suitable for sample and standard preservations. Reagent grade nitric acid may be used, if the absence of metals of interest is verified experimentally.

6.3 Standards - Stock commercial 1000 µg/ml metal solution standards in inert plastic containers are acceptable for preparing working standards by serial dilutions. All blanks and working standards are preserved with 0.5%

concentrated nitric acid. All standards at concentrations less than 1 µg/ml are prepared fresh daily.

7. OPERATION

7.1 Instrumental - The analyst should follow the manufacturer's instructions on installation, alignment and optimization of the instruments. Suggested instrumental settings are presented in Table II. These are, however, not invariant, and the Perkin-Elmer furnace manual (1) should be consulted for equipment maintenance, analytical line selection, charring and atomization temperatures, and expected absolute sensitivities. Perkin-Elmer hollow cathode lamps are used for the determination of beryllium, lead and silver, and the EDLs, due to their higher energy outputs and thus better signal to noise ratios, are recommended for the antimony, arsenic, cadmium, selenium and tellurium analyses. Scale expansion, consistent with the limitations of instrumental background noise, and the gas interrupt feature of the furnace controller are acceptable means of signal attenuation, and are used extensively for low level metal determinations.

7.2 Procedure

7.2.1 Prepare a reagent blank and at least 2 working standards for the concentration range of interest and analyze these under previously established instrumental conditions. Assess the colinearity of standards and blank graphically and verify that the calibration curve (peak height vs. concentration) passes through the origin.

7.2.2 Manually agitate the sample container and with an Eppendorf pipet inject samples and standards into the furance tube. The data points provide standard addition curves for the evaluation of element concentrations. Keep total volume injected constant at less than 100 µl and the acidities invariant for each analysis.

7.2.3 Sample concentrations outside the linear range of the previously determined calibration curve must be diluted or smaller sample volumes taken for analysis. The determined metal content should be lower than the concentration of the highest working standard.

8. COMPUTATION

The method of standard additions is used for the evaluation of element concentrations. A sample and at least two sample spikes are analyzed. Peak heights vs. amount of element added are plotted and the colinear graph is extrapolated to the intersection with the concentration axis. The numerical value of this intercept is the determined concentration. Each sample that is suspect or is shown to have matrix variations must be analyzed individually by standard additions. The analyses of surface waters free of gross pollution and nearly constant in composition, i.e. Great Lake water, have shown that working curves remain linear and invariant in slopes, and thus standard additions on each sample are not required. However, the performance of the graphite tube and other experimental variables must be monitored by the redetermination of standard curves on approximately 10% of the samples.

9. COMPARATIVE DATA

Tables III, IV and V summarize comparative data for the graphite furnace and the appropriate NPDES approved methods on representative effluent samples. Each set of results represents a separate outfall that had been spiked at a concentration measurable by flame atomic absorption spectrophotometry for beryllium, cadmium, lead and silver and the hydride generation method for arsenic and selenium. This range is above the optimum concentration for the flameless atomization method, and the reported results reflect the use of either smaller sample aliquots or appropriate dilutions. In addition, the listed furnace data were obtained on undigested samples, and thus demonstrate that aqueous solutions can be analyzed with good precision and accuracy in the presence of suspended solids.

Antimony and tellurium are included in this request, since these metals are known to be toxic and the approved flame atomic absorption method for antimony with a sensitivity of 0.5 mg/ml(2) exceeds the recommended level (3) of 0.2 mg/ml in a marine environment. Tellurium is not included in the NPDES parameter list; however, its concentration should be of interest in environmental monitoring applications. Table VI documents satisfactory recoveries for antimony, arsenic, selenium and tellurium in different effluent matrices.

Table VII summarizes experimental precision data for all metals under study.

10. APPLICABILITY

10.1 Industrial and Municipal Outfalls - The proposed method, due to its high sensitivity, does provide for a more complete characterization of these outfalls. This is particularily true for those elements, i.e. Pb, Cd, that have effluent permit limitations near the detection limit of standard flame atomic absorption techniques. In addition, the method does allow for an independent varification of element concentrations determined by other NPDES approved methods. This technique is documented in the literature (4,5) for environmental monitoring of effluents.

10.2 Surface Waters - In view of the low metal concentrations generally found in surface waters, a sensitive, precise method is needed to determine baseline contaminant concentrations. The flameless atomization method is ideally suited for this purpose and will be used extensively for the assessment of water quality in these environments. Several publications (6,7,8) discuss this area of applicability.

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* The use of a company name is for identification purposes only and does not constitute an endorsement by the U.S. EPA.

TABLE I

Spectrophotometer Settings and Linear Ranges

Element	Wavelength, nm	Bandpath, nm	Linear Range, µg/l
Ag	328.1	0.7	0.5 - 10.0
As	193.7	0.7	1 - 40
Be	234.9	0.7	1 - 20
Cd	228.8	0.7	0.2 - 3.0
Pb	283.3	0.7	1 - 30
Sb	217.6	0.2	1 - 20
Se	196.0	0.7	1 - 20
Te	214.3	0.7	1 - 20

TABLE II

Furnace Operating Parameters

Element	Gas Flow, ml/min	Drying Temp., °C (Time, sec.)	Charring Temp., °C (Time, sec.)	Atomization Temp °C (Time, sec.)
Ag	50	125 (60)	850 (20)	2500 (5)
As	50	125 (60)	1000 (40)	2700 (5)
Be	50	125 (60)	1200 (30)	2700 (5)
Cd	50	125 (60)	400 (20)	2100 (3)
Pb	50	125 (60)	700 (30)	2700 (3)
Sb	50	125 (60)	1000 (40)	2200 (5)
Se	50	125 (60)	1000 (40)	2700 (3)
Te	50	125 (60)	700 (40)	2700 (5)

TABLE III

Comparative Data for Arsenic and Selenium

Sample No.	Matrix Type	As, µg/l		Se, µg/l	
		Hydride	Furnace	Hydride	Furnace
408	Metals Industry	14	16	14	13
428	Metals Industry	12	12	14	14
436	Metals Industry	28	24	13	16
448	Metals Industry	13	16	14	14
452	Metals Industry	12	13	12	13
594	Metals Industry	20	20	11	13
6000	Power Plant Industry	10	14	11	12
6039	Power Plant Industry	12	14	12	11
6046	Power Plant Industry	12	14	13	12
6073	Power Plant Industry	12	14	13	15
3314	Indust. & Municipal Wastes	12	10	13	13
3315	Indust. & Municipal Wastes	14	10	12	15
3323	Indust. & Municipal Wastes	12	11	13	10
3324	Indust. & Municipal Wastes	10	11	12	11
3328	Indust. & Municipal Wastes	12	10	13	12
3329	Indust. & Municipal Wastes	12	10	13	11

TABLE IV

Comparative Data for Silver and Beryllium

Sample No.	Matrix Type	Ag, µg/l		Be, µg/l	
		Flame AA	Furnace AA	Flame AA	Furnace AA
404	Metals Industry	19	21	21	19
432	Metals Industry	21	17	19	19
440	Metals Industry			21	20
444	Metals Industry	21	16	20	20
464	Metals Industry	21	24	20	20
6026	Power Plant Industry	21	19	21	19
6050	Power Plant Industry	21	21	21	19
6057	Power Plant Industry	21	21	21	19
6064	Power Plant Industry	20	26	21	18
3261	Indust. & Municipal Wastes	21	18	21	20
3263	Indust. & Municipal Wastes	21	18	20	18
3265	Indust. & Municipal Wastes	40	45	19	19
3267	Indust. & Municipal Wastes	29	30	20	19
3333	Indust. & Municipal Wastes	20	24	21	21
3334	Indust. & Municipal Wastes	21	20	22	20

TABLE V

Comparative Data for Cadmium and Lead

Sample No.	Matrix Type	Cd, µg/ml		Pb, µg/ml	
		Flame AA	Furnace AA	Flame AA	Furnace AA
404	Metals Industry	21	20	100	105
432	Metals Industry	21	21	120	105
440	Metals Industry	20	19	110	135
444	Metals Industry	21	22	120	130
464	Metals Industry	20	20	105	100
6026	Power Plant Industry	21	22	94	100
6050	Power Plant Industry	20	22	94	100
6057	Power Plant Industry	20	22	120	105
6064	Power Plant Industry	21	21	120	110
3261	Indust. & Municipal Wastes	20	21	130	135
3263	Indust. & Municipal Wastes	25	26	130	120
3265	Indust. & Municipal Wastes	24	26	110	120
3267	Indust. & Municipal Wastes	23	23	130	120
3333	Indust. & Municipal Wastes	24	22	120	110
3334	Indust. & Municipal Wastes	22	25	110	95

TABLE V/

Recovery of Arsenic, Antimony, Selenium
And Tellurium from Environmental Samples

Type of Sample	Conc. of Metals Added, µg/l	As, µg/l			Sb, µg/l			Se, µg/l			Te, µg/l		
		Initial	Final	Rec.,%	Initial	Final	Rec.,%	Initial	Final	Rec,%	Initial	Final	R
tals Industry	10.0	<1.0	10.5	105	<2.0	10.0	100	1.0	11.0	100	<1.0	10.0	
	10.0	13.0	22.0	90	5.0	14.5	95	3.0	14.0	110	2.0	12.5	
	10.0	3.0	12.0	90	<2.0	10.0	100	4.0	15.0	110	<1.0	9.5	
	10.0	1.0	10.5	95	<2.0	9.5	95	<1.0	9.5	95	<1.0	9.0	
wer Plant	10.0	2.5	13.0	105	3.0	12.0	90	3.0	13.0	100	<1.0	10.0	
	10.0	1.0	11.0	100	<2.0	10.0	100	1.0	11.0	100	<1.0	10.5	
	10.0	1.0	10.0	90	<2.0	10.0	100	1.0	11.0	100	<1.0	10.0	
	10.0	1.5	10.5	90	<2.0	9.5	95	1.0	12.0	110	<1.0	10.5	
wage Treatment lant	10.0	2.0	11.0	90	4.0	13.0	90	4.0	14.0	100	2.0	12.0	
	10.0	2.0	12.0	100	3.0	12.5	95	<1.0	10.0	100	2.0	13.0	
	10.0	2.0	11.0	90	3.0	12.0	90	<1.0	10.0	100	<1.0	9.5	
	10.0	2.0	12.0	100	3.0	13.5	105	6.0	15.5	95	2.0	11.5	
nsitivity, g(absolute)			3.0×10^{-11}			3.0×10^{-11}			5.0×10^{-11}			4.0×10^{-11}	
.L.[a], µg/l (relative)			0.5			2.0			2.0			1.0	

[a]D.L.: detection limit ; defined as signal:noise = 2

TABLE VII

Precision of the Flameless Atomization Method

Element	Concentration, µg/l	n	S.D., µg/l	Rel.S.D., %
Ag	21.0	10	1.0	4.8
As	2.5	12	0.2	8.0
	10.0	16	0.3	3.0
Be	19.1	10	0.6	3.1
Cd	1.5	10	0.1	6.7
	27.2	10	1.4	5.1
Pb	8.9	10	0.4	4.5
	105	10	5	4.8
Sb	2.5	15	0.1	4.0
	10.0	15	0.3	3.0
Se	3.0	8	0.2	6.7
	10.0	13	0.5	5.0
Te	2.5	15	0.1	4.0
	10.0	15	0.4	4.0